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Synthetic CaO-based Sorbent for CO_2 Capture

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Abstract

The capture and purification of carbon dioxide (CO_2) from flue or fuel gas underlies the cost efficiency of carbon capture and storage (CCS) applications in the power and industrial sectors and there is considerable scope for cost reduction with the development of novel capture technologies. High-temperature sorbents are seen as a "next-generation" technology and a promising candidate is calcium oxide (CaO) derived from natural limestone, which is used in a process known as carbonate looping. This process exploits the reversible reaction between CaO and CO_2 to form calcium carbonate ($CaCO_3$).

Unfortunately, sorbent derived from natural limestone loses its capacity to capture CO_2 through long-term cycling, and a large amount of fresh limestone is required to maintain an acceptable CO_2 capture efficiency. This work describes the development and characterisation of synthetic CaO-based sorbents, such as those incorporating a mixed calcium-aluminium oxide binder—in this case produced by precipitation in a slurry bubble column. Reactivity tests using a thermogravimetric analyser (TGA) demonstrate the improved long-term CO_2 uptake of the synthetic sorbent. The highest CO_2 uptake observed after 30 cycles was achieved with 85 wt.% CaO and binder, which was three times higher than the observed capacity of a natural limestone (Havelock). However, contrary to TGA results, experimental results for reactivity tests conducted using a bench-scale fluidised bed reactor (FBR) showed the highest uptake for the precipitated sorbent with no binder. A decrease in uptake was observed corresponding an increase in binder loading from 0–25 wt.%, which was coupled with an increase in mass loss owing to elutriation, attributed to decrepitation during cycling.

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1. Introduction

The global deployment of carbon capture and storage (CCS) is essential if we are to continue to use fossil fuels and hope to achieve large-scale global CO_2 emissions reductions in the next 30–40 years. CCS may be seen as transitional technology offering a near-term way of mitigating climate change because transforming the existing energy system to a low-carbon energy system is likely to take many decades. Cost reduction is a major challenge for the CCS technology and the capture step is the most expensive part of the process owing to a considerable parasitic energy demand (whereby about 20–30 % more fuel is needed to achieve the same output of power). Next generation capture technologies offer the potential to improve overall efficiency and reduce the cost of CO_2 capture when compared with current market-leading technologies, i.e., amine-based solvent-scrubbing.

High-temperature solid-looping using calcium oxide (CaO) is a promising capture process, known as "carbonate looping". This process is based on the reversible gas-solid reaction between CaO and CO_2 to form calcium carbonate ($CaCO_3$) (Equation 1). The forward reaction (carbonation) can be used to remove CO_2 from a mixture of gases, and when heat is applied to the $CaCO_3$ the CO_2 can be released via the reverse reaction (calcination), and the CaO regenerated. A near pure stream of CO_2 can be produced if the calcination reaction is carried out under a high CO_2 partial pressure at about 900–950 °C. To achieve this high temperature, it is proposed that additional fuel be combusted in pure O_2, requiring an air separation unit [1,2] (Figure 1).

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \qquad \Delta H_{r,298K} = -178 \text{ kJ/mol} \qquad (1)$$

Figure 1 shows a simplified process flow diagram of the carbonate looping technology. The major difference between high-temperature capture process and conventional low-temperature processes is that the energy penalty (largely associated with sorbent regeneration, which includes air separation in the case of the carbonate looping) is partially offset by the potential to recuperate heat at high temperature (≥ 650 °C) that may be used to generate additional steam. Thus, the theoretical efficiency penalty associated with CO_2 capture from a power station using carbonate looping is only 6–8 % [3], compared to about 10–12 % for amine-based solvent-scrubbing [4]. Other advantages of carbonate looping include: the synergy with the cement industry with the potential to decarbonise cement manufacture and power generation; relatively low scale-up risks with the use of mature circulating fluidized bed technology; and applicability to pre-combustion capture for electricity and/or hydrogen (H_2) synthesis [5–8].

Sorbent derived from natural limestone loses its capacity to capture CO_2 after multiple CO_2 capture-and-release cycles, and a large amount of fresh limestone is required to maintain an acceptable CO_2 capture efficiency [1,9,10]. The main factors influencing this drop-off in uptake are: sintering, attrition, and chemical deactivation owing to the competing chemical reaction with sulfur dioxide (SO_2)—these factors are discussed in detail in a recent review by Blamey et al. [11].

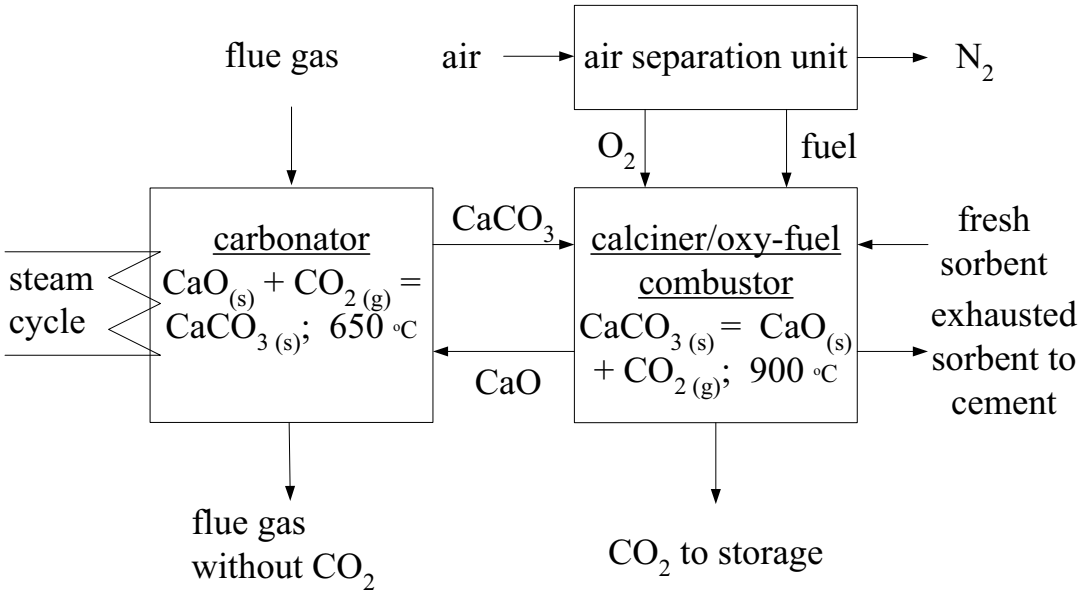


Figure 1. Simplified process flow diagram of carbonate looping for CO_2 removal from flue gas

Synthetic CaO-based sorbents, capable of maintaining a high CO_2 uptake, offer the potential to improve the cost efficiency and future viability of carbonate looping. One particularly promising category of synthetic CaO-based sorbents use solid binders e.g.: Al_2O_3 [12–15] and $CaTiO_3$ [16] which provide a solid matrix to support the reactive CaO. The main idea behind using a binder is to reduce reactivity decay owing to morphological changes associated with sintering, and to improve the mechanical stability for use in FBRs. However, susceptibility to the competing reaction with SO_2 remains an issue [17]. Li et al [14,15] demonstrated improved long-term reactivity with a CaO mixed with a mixed Ca-Al oxide (mayenite) produced by a hydrolysis technique; and more recently, Manaovic and Anthony [13] showed that similar improvements could be obtained by simply grinding calcined limestone with cement powders. In view of such promising results this work describes a novel mixed-precipitation method using a slurry bubble column to achieve mixing of the sorbent and binder at the micro-grain scale. This work also follows previous studies published by Gupta and Fan [18] and more recently Florin and Harris [19] which showed CaO-based sorbents derived from precipitated $CaCO_3$ ("PCC") to be highly reactive compared to those derived from natural limestones, although highly susceptible to sintering. In this work we describe the mixed-precipitation method to produce $CaCO_3$ and $Al(OH)_3$ (as a precursor to synthetic CaO-based sorbent incorporated with mixed calcium-aluminum binder); and report results demonstrating improved long-term carrying capacity based on experiments conducted in a thermogravimetric analyzer (TGA) and a bubbling fluidized bed reactor (BFB).

2. Experimental

Precipitation experiments were carried out using a slurry bubble column (i.d. 50 mm) with a sintered glass distributor with average porosity of 70 μm (Figure 2). A saturated slurry (15 times the saturation limit) of $Ca(OH)_2$ (Acros Organics, purity > 98 wt.%) was loaded in the column under a flow of N_2. $Al(NO_3)_3.9H_2O$ (Fisher Scientific, purity > 98 wt. %) was introduced in order to achieve a determined $CaCO_3$-to-$Al(OH)_3$ ratio and this mixture was held under N_2 before the precipitation of $CaCO_3$ was initiated by switching the N_2 to the same flowrate of CO_2,

which was bubbled through the slurry for five minutes. When CO_2 is bubbled through the slurry, some of the gas dissolves to form carbonate ions (CO_3^{2-}) that react with the Ca^{2+} and precipitate out as $CaCO_3$.As the Ca^{2+} ions are consumed they are replenished by the continual dissolution of $Ca(OH)_2$ until this supply is depleted. At the beginning of the experiments, when the OH^- concentration is high, the Al^{3+} ions are likely present in complex form (e.g., $Al(OH)_4^-$) which reacts with H^+ ions and precipitates out as $Al(OH)_3$ as the pH drops from 12 to about 6 when all the $Ca(OH)_2$ is converted to $CaCO_3$.The mixed precipitate, consisting mainly of $CaCO_3$ and $Al(OH)_3$, was collected and transferred directly to an oven at 120 °C for drying overnight. For reactivity testing in the TGA the dried filter cake was crushed into a fine powder using a mortar and pestle; for experiments in the BFB particles were sieved to 500–710 μm. Sorbent preparation for the BFB experiments also included a thermal pre-treatment step carried out in a tube furnace. This involved heating to 500 °C under N_2 to decompose the nitrate residues and convert $Al(OH)_3$ to Al_2O_3. An additional thermal pre-treatment step that involved heating to 950 °C under N_2 for a duration of three hours (to convert CaO and Al_2O_3 to mixed Ca-Al oxides), was also used for select experiments. Good experimental repeatability of the precipitation procedure was determined by conducting two repeats of the mixed precipitation and testing the reactivity in the TGA.

Reactivity testing was carried out using a TGA (PerkinElmer Pyris 1 TGA) and a bench-scale BFB reactor. TGA tests used about 5 mg of sample, carbonation was carried out at 650 °C (10 minutes) and calcination at 900 °C (5 minutes), both under an atmosphere of 15 % CO_2 in N_2 and He (The TGA was set up with two inert gases, N_2 was fed directly to the furnace and He was directed via the balance before entering the furnace), with a total gas flowrate of about 130 mL/min. A heating rate of 50 °C/min was used to vary the temperature from 650–900 °C for up to 30 CO_2 capture-and-release cycles, with the reactivity measured by recording the change in sample weight. (An increase in sample weight corresponds to carbonation and a decrease in sample weight corresponds to calcination.) These calcination/carbonation measurements were used to describe the CO_2 uptake or "carrying capacity" of the sorbent expressed in terms of conversion (X), defined as moles of CO_2 captured per moles of CaO and/or g-CO_2 per g-of calcined sorbent. In atypical experiment the material was loaded into the reactor as a mixture of mainly $CaCO_3$ and $Al(OH)_3$ and upon heating to 900 °C four distinct weight loss events were observed: The first weight loss is associated with the removal of physically bound water commencing at about 80 °C; the second decomposition at about 150 °C is likely associated with the decomposition of nitrate residues; this is followed by the decomposition of $Al(OH)_3$ to Al_2O_3 at around 300 °C; and the fourth weight loss is due to the calcination of $CaCO_3$. Finally, the solid-state reaction between CaO and Al_2O_3 to form mixed calcium-aluminum oxides (e.g., mayenite, $Ca_{12}Al_{14}O_{33}$) – a process not accompanied by a weight change – results in the formation of an inert solid binder [14,15]. In the TGA, this process is thought to occur during the first five calcination steps, when the temperature is > 800 °C [15], corresponding with an irreversible consumption of a stoichiometric amount of CaO. Complete conversion of Al_2O_3 to mayenite was assumed when determining the initial loading of $Al(NO_3)_3.9H_2O$. The BFB reactor consisted of a resistance heated furnace surrounding a quartz reaction vessel (2.1×10^{-2} m, i.d.). A detailed description of the experimental setup can be found elsewhere [20]. Consistent with the TGA experiments, carbonation was conducted at 650 °C and calcination at 900 °C, both under 15 % CO_2 in N_2. The fluidizing/reactive gas (cold flowrate 47.5 cm^3/s, U/Umf =8) was first preheated by flowing through a quartz wool plug upstream from a sintered quartz distributor. A fraction of the off-gas was continuously sampled and the CO_2 concentration measured (using an infrared gas analyzer). The mechanical stability of the limestone particles were evaluated by measuring the total bed loss during an experiment.

3. Results and Discussion

It was hypothesised that the presence of an inert solid binder would improve the long-term carrying capacity by decreasing the rate of sintering (as well as improving the mechanical stability–discussed below with reference to the BFB experimental results). The extent by which the presence of binder reduces the rate of sintering is shown in Figure 2a which compares the decay in conversion (X) through 30 cycles for the synthetic sorbent with binder loading from 0–25 %. The performance of a natural limestone (Havelock) is also shown as a benchmark. An optimal binder loading of 15 % was observed; increasing the amount of binder to 25 % led to a decrease in the long-term conversion and no significant improvement (within the range of experimental variability) is observed with a binder loading of 5 %, compared to the pure PCC. The decay profile through for the synthetic sorbent in the first 3–4 cycles follows a different trajectory compared to the natural limestone and the PCC owing to the formation of the mixed Ca-Al oxide. There is a trade-off because as the amount of binder is increased there is a corresponding decrease in the amount of reactive CaO. Hence, in Figure 2b, we compare the carrying capacity expressed in terms of g-CO_2 per g-of calcined sorbent, clearly showing the superior carrying capacity of the synthetic sorbent (about three times the capacity of the natural limestone after 30 cycles). An optimal binder loading of about 15 wt.% is consistent with the literature [12–15].

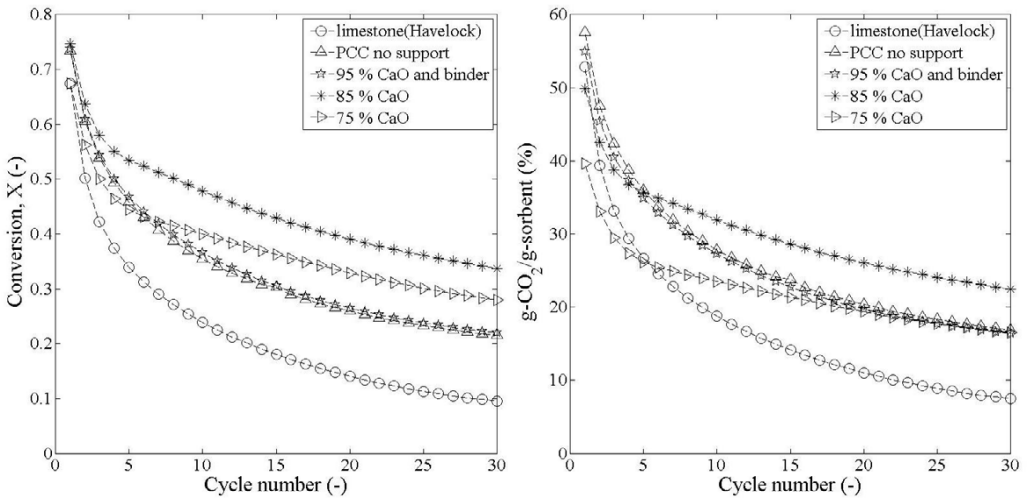
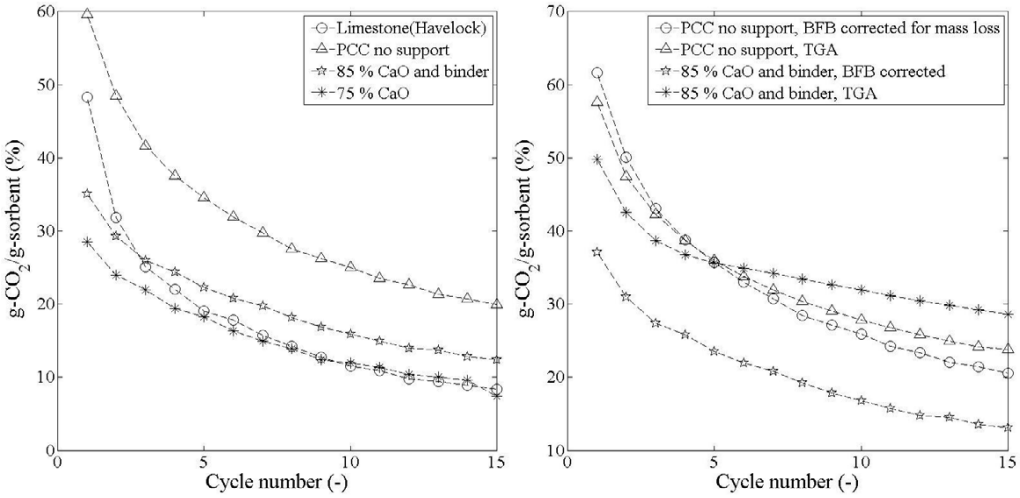


Figure 2. Carrying capacity through 30 CO_2 capture-and-release cycles of synthetic CaO-based sorbents with binder loading from 0-25 wt. % and compared with natural limestone (Havelock), expressed in terms of: (a) conversion, X; and (b) g-CO_2 per g-calcined sorbent

BFB experiments were conducted to assess the mechanical stability of the synthetic sorbent. Dissimilar to the TGA experiments, in the BFB, the sorbent is exposed to abrasive conditions and any small particles formed during experiments may be elutriated from the reactor. A number of different mechanisms are expected to lead to the formation of small particles: Primarily, attrition, which is the formation of fine particles abraded from the particle surface due to particle collisions with reactor walls and other particles. These small particles are likely to be elutriated and thus results in a decrease in the amount of reactive bed material. Decrepitation refers to the fragmentation of particles due to internal stresses associated with heating, devolatilisation, and/or

chemical reaction. These processes produce new surface susceptible to abrasion and may also result in the direct formation of fine particles that may be small enough to be elutriated. The importance of the different mechanisms is likely to be affected by a wide range of factors including properties of the sorbent and properties of the experiment apparatus, the likely importance of the different mechanisms are discussed below.

As mentioned above, it was hypothesized that the presence of the binder would improve the mechanical stability of the sorbent and that synthetic sorbent with larger amounts of binder would be most resistant to attrition and decrepitation. Surprisingly, experimental results conducted in the BFB showed a decrease in the carrying capacity at 15 cycles corresponding with an increase in binder loading from 0–25 % (Figure3a). The decrease in capacity was coupled with an increase in the amount of bed material lost owing to elutriation from 3 % to 15 % after 15 cycles, for PCC with no binder and synthetic sorbent with 25 wt.% binder, respectively. Figure 3b compares TGA with BFB results with the latter data set also given with a correction made for mass loss. In the case of the 85 % CaO it is clear that the difference in the carrying capacity is not solely due to the loss of reactive material. The dramatic decrease in the capture capacity of the CaO with binder from the TGA to BFB suggests that the structural changes during the solid-state mixed oxide reaction are very significant in terms of the subsequent reactivity of the sorbent. It is suspected that the more gradual heating of the powdered samples in the TGA results in more stable formation of crystals of the mixed Ca-Al binder owing to the longer time for crystal growth. This is consistent with previous work by Li et al.[15] that highlighted the effect of the temperature of a thermal-pre-treatment step (during which mayenite is formed) on the subsequent reactivity of their synthetic sorbents. Thus, to investigate the significance of the thermal history we subjected the synthetic sorbent with 85 wt. % CaO to different thermal pre-treatments, i.e., “cold loading” at 900 °C, a slow-ramp (1 °C/s) from room temperature to the calcination temperature (900 °C), and a thermal pretreatment in a tube furnace at 950 °C for three hour under N_2. No significant difference in the CO_2 carrying capacity, nor amount of bed loss was observed when comparing the synthetic sorbent loaded cold with the slow-ramp experiment suggesting that decrepitation associated with an initial “thermal shock” is not responsible for the loss of bed material (Figure 4). We note that the slow heating rate is comparable with the heating rate used for the TGA experiments, however better heat transfer in the BFB is still expected to increase the rate of mixed calcium-aluminum oxide crystal formation, consistent with the different decay trajectories between the TGA and BFB (Figure 3b). The synthetic sorbent subjected to the thermal pretreatment displays a significantly diminished carrying capacity in the first 5–10 cycles consistent with complete “ex-situ” formation of the mixed Ca-Al binder and/or pre-sintering, however by the 15th cycle the capacity is consistent with the other samples. These results suggest that the decay in the carrying capacity of the synthetic sorbent is due to mechanical stresses associated with calcination/carbonation likely related to the Ca-Al crystal structure. The relatively small loss of bed material in the case of the CaO derived from precipitated $CaCO_3$ without binder may be due to a greater susceptibility to sintering which would impart a greater resistance to decrepitation and attrition by cementing the CaO grains together.



(a) (b)

Figure 3. (a) Carrying capacity of CaO with varying amounts of binder and compared with Havelock in a bench-scale BFB; (b) Comparison between BFB and TGA with BFB results corrected for mass loss owing to elutriation of fine particles

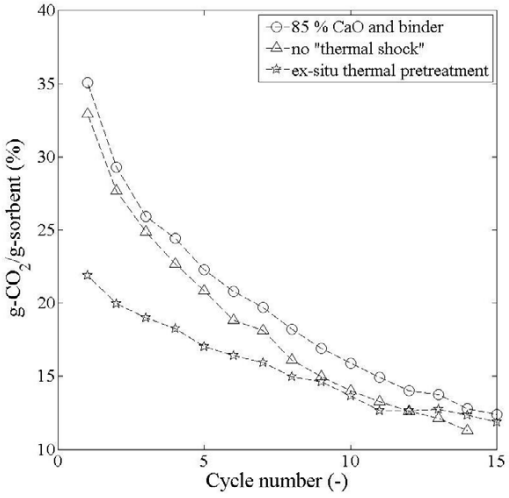


Figure 4. The effect of thermal history on the carrying capacity of 85 % CaO in BFB

4. Conclusions

We observed an improved carrying capacity using a synthetic CaO-based sorbent with a mixed calcium-aluminum binder, and identified an optimal binder loading of 15 wt.% based on reactivity tests conducted in a TGA – consistent with the literature. However, in BFB the CaO with no binder showed the highest carrying capacity; and we observed a significant decrease in the carrying capacity corresponding with an increase in the binder loading from 0–25 wt. %

coupled with an increase in the amount of bed material elutriated with the higher binder loadings. Experiments carried out investigating the influence of the thermal history suggest that the decay in the carrying capacity of the synthetic sorbent may be related to mechanical stresses during calcination/carbonation which exploit weaknesses in the Ca-Al crystal structure. Further work is required to better elucidate these results.

5. References

[1] Shimizu T.; Hirama T.; Hosoda H.; Kitano K.; Inagaki M.; Tejima, K. A twin fluid-bed reactor for removal of CO_2 from combustion processes. *Trans. IChemE* 1999; 77A: 62–68
[2] Abanades, J.C.; Anthony, J.E.; Lu, D.Y.; Salvador, C.; Alvarez, D. Capture of CO_2 from combustion gases in a fluidised bed of CaO. *AIChE J.* 2004, 50, 1614–1622
[3] Abanades, J.C.; Anthony, E.J.; Wang, J.; Oakey, J.E. Fluidized bed combustion systems integrating CO2 capture with CaO. *Environ. Sci. Technol.* 2005, 39(8), 2861–2866
[4] UK Advanced Power Generation Technology Forum (APGTF), report titled: Cleaner Fossil Fuel Power Generation in the 21st Century, published April 2009, available from http://www.apgtf-uk.com/
[5] Han, C.; Harrison, D. Simultaneous Shift Reaction and Carbon Dioxide Separation for the Direct Production of Hydrogen. *Chem. Eng. Sci.* 1994, 49, 5875–5883
[6] Balasubramanian, B.; Lopez Ortiz, A.; Kaytakoglu, S.; Harrison, D.P. Hydrogen from methane in a single-step process. *Chem. Eng. Sci.* 1999, 54, 3543–3552
[7] Lin, S-Y.; Harada, M.; Suzuki, Y.; Hatano, H. Developing an innovative method, HyPr- RING, to produce hydrogen from hydrocarbons. *Energy Conv. Man.* 2002, 43, 1283–1290.
[8] Gao, L.; Paterson, N.; Dugwell, D.; Kandiyoti, R. Zero-emission carbon concept (ZECA): Equipment commissioning and extents of the reaction with hydrogen and steam. *Energy Fuels* 2008, 22(1), 463–470
[9] Curran GP, Fink CE, Gorin E. CO_2 acceptor gasification process. In F. C. Schora Symposium chairman. Fuel Gasification; American Chemical Society: Washington, D.C; 1966, p. 141
[10] Barker R. The reversibility of the reaction $CaCO_3 \rightarrow CaO + CO_2$. Journal of Applied Chemistry and Biotechnology 1973; 23: 733–742
[11] Blamey, J.; Anthony, E.J.; Wang, J.; Fennell, P.S The Carbonate Looping Cycle for Large-Scale CO_2 Capture. *Prog. Energy Comb. Sci.* 2010, 36(2), 260–279[12] Pacciani R, Muller CR, Davidson JF, Dennis JS, Hayhurst AN. Synthetic Ca-based solid sorbents suitable for capturing CO_2 in a fluidised bed. The Canadian Journal of Chemical Engineering 2008, 86, 356–366
[13] Manovic, V.; Anthony, E.J. CaO-based pellets supported by calcium aluminate cements for high-temperature CO2 capture. *Enviro. Sci. Technol.* 2009, 43, 7117–7122
[14] Li, Z-s.; Cai, N-s.; Huang, Y-y.; Han, H-j. Synthesis, Experimental studies, and analysis of a new calcium-based carbon dioxide absorbent. *Energy Fuels* 2005, 19, 1447–1452
[15] Li, Z-s.; Cai, N-s.; Huang, Y-y. Effect of preparation temperature on cyclic CO_2 capture and multiple carbonation-calcination cycles for a new Ca-based CO_2 sorbent *Ind. Eng. Chem. Res.* 2006, 45, 1911–1917
[16] Aihara M, Nagai T, Matushita J, Negishi Y, Ohya H. Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/decarbonation reaction. *Appl. Energy* 2001; 69: 225–238]
[17]Manovic V, Anthony EJ. Sulfation performance of CaO-based pellets supported by calcium aluminate cements designed for high temperatureCO2 capture. *Energy Fuels* 2010;24:1414–1420
[18] Gupta, H.; Fan, L-S. Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas *Ind. Eng. Chem. Res.* 2002, 41, 4035–4042
[19] Florin, N.H.; Harris, A.T. Screening CaO-Based Sorbents for CO_2 Capture in Biomass Gasifiers. *Energy Fuels* 2008, 22, 2734–2742

[20] Blamey, J.; Paterson, N.; Dugwell, D.; Fennell, P.S. Mechanism of particle breakage during reactivation of Ca)-based sorbents for CO_2 capture *Energy Fuels* 2010, 24, 4605–4616